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CRYSTAL-STRUCTURE REFINEMENT OF BOROMUSCOVITE POLYTYPES USING A COUPLED RIETVELD – STATIC-STRUCTURE ENERGY-MINIMIZATION METHOD

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ABSTRACT

Boromuscovite from a granitic pegmatite at Řečice, Czech Republic, occurs only as very fine-grained aggregates, and is a mixture of $2M_1$ and $1M$ polytypes. Crystal structures of both polytypes have been simultaneously refined in space groups $C2/c$ and $C2/m$, respectively, using a coupled Rietveld – static-structure energy-minimization method. Intensity data were collected on a high-resolution powder diffractometer in transmission geometry, with the sample prepared such that preferred orientation is largely avoided. The refinement converged to R_{wp} = 13.8% (R_{exp} = 7.9%), R_{BRG} ($2M_1$) = 3.8%, and R_{BRG} ($1M$) = 3.8%. Boron is evenly distributed between the two polytypes, and <*T*–O> distances correspond well with the B-content at the corresponding *T*-sites.

Keywords: boromuscovite, Rietveld structure refinement, chemical analysis, polytype, energy minimization.

SOMMAIRE

La boromuscovite provenant d'une pegmatite granitique à Řečice, en République Tchèque, se présente sous forme d'agrégats à granulométrie très fine, formés d'un mélange des polytypes $2M_1$ et $1M$. Les structures cristallines de ces polytypes ont été affinées simultanément dans les groupes spatiaux $C2/c$ et $C2/m$, respectivement, en utilisant une méthode couplée impliquant un affinement Rietveld et une minimisation de l'énergie de la structure statique. Les données d'intensité ont été mesurées par diffractométrie sur poudre à haute résolution, en mode transmission, avec précautions spéciales pour minimiser les effets dus à l'orientation préférentielle des grains. L'affinement a atteint un résidu R_{wp} = 13.8% (R_{exp} = 7.9%), R_{BRG} ($2M_1$) = 3.8%, et R_{BRG} ($1M$) = 3.8%. Le bore est également présent dans les deux polytypes, et les distances <*T*–O> correspondent bien aux teneurs en bore des sites *T* correspondants.

(Traduit par la Rédaction)

Mots-clés: boromuscovite, affinement Rietveld de la structure, composition chimique, polytype, minimisation de l'énergie.

INTRODUCTION

Boromuscovite was described as a new mineral species by Foord *et al.* (1991) from the Little Three mine, California, and has rince been found at Řečice, Czech Republic (Novák *et al.*, unpubl. data). It has an ideal formula $KAl_2(Si_3B)O_{10}(OH)_2$, and the chemical composition reported by Foord *et al.* (1991) is very close to that of the end-member; the key chemical feature is the occurrence of a significant amount of B at the tetrahedral site(s) of the structure. However, no crystal-structure refinement has yet been done because of the fine-grained nature of the mineral. Furthermore, boromuscovite occurs as a mixture of $1M$ and $2M_1$ polytypes, further complicating the problem of structural characterization.

Rietveld refinement is an effective method to characterize the crystal structures of fine-grained materials. However, refinement can sometimes be difficult or even unreliable when the structure is complex or when there is insufficient resolution in the powder-diffraction data. It had been shown (Liang &

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Hawthorne 1994) that such problems can be ameliorated by coupling Rietveld structure-refinement with static-structure energy minimization (designated as the *coupled method* in subsequent text). The coupled method incorporates crystal energetics into the structure-refinement procedure, and hence constrains the refinement process in a fashion similar to the use of soft bond-distance constraints. It will be shown here that the crystal structure of the boromuscovite polytypes can be determined successfully using the coupled method.

The Coupled Rietveld – Static-Structure Energy-Minimization Method

The coupled method involves two aspects of crystal-structure study: (1) the powder-diffraction experiment and Rietveld refinement of the experimental data, and (2) the static-structure energy calculation. The core of the method is to minimize the weighted sum of two quantities: (1) the difference between the observed and calculated powder-diffraction patterns, and (2) the static-structure energy. The quantity to be minimized in a Rietveld refinement is

$$\mathfrak{R} = \Sigma \mathrm{w_i}(Y_{\mathrm{io}} - Y_{\mathrm{ic}}) \tag{1}$$

in which Y_{io} and Y_{ic} are the observed and calculated step-intensities, respectively. The step-intensity – weighted-difference, $\mathfrak{R}_{wp}$, which is another quantity available in Rietveld refinement, is used in the coupled method:

$$\mathfrak{R}_{wp} = \frac{\mathfrak{R}}{\Sigma \mathrm{wi\ Yio}} \tag{2}$$

The static-structure energy is calculated as a sum of several separate terms, under the additive assumption of structure energy (Catlow 1990, Burnham 1990). The Coulombic interaction has the form

$$U_{\mathrm{c}} = \frac{q_i\, q_j}{r_{ij}} \tag{3}$$

in which q_i and q_j are the formal charges of atom pair *i* and *j*, respectively, and r_{ij} is the interatomic distance. The repulsion is expressed using the Born-type potential (Born & Huang 1954)

$$U_R = \lambda_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) \tag{4}$$

in which λ_{ij} and ρ_{ij} are atom-pair-specific parameters (repulsion parameters), which are determined empirically (Kunz & Armbruster 1992) or semi-empirically (Post & Burnham 1986). In order to model more closely the repulsion involving Si and O atoms, the Buckingham potential is used for these atoms:

$$U_R = \lambda_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) + C_{ij} r_{ij}^{-6} \tag{5}$$

The extra coefficient in (5), C_{ij}, is atom-pair selective, and can be determined as for λ_{ij} and ρ_{ij}.

Extensive work (Sanders *et al.* 1984) has shown that covalency can be accounted for by including bond-bending and polarization terms. The bond-bending effect is expressed as the harmonic potential function

$$U_B = k_B(\theta_i - \theta_0)^2 \tag{6}$$

in which k_B is constant for all O–Si–O bond-bending systems, and $(\theta_i - \theta_0)$ is the deviation of the O–Si–O (or O–Al–O) angle in the structure from that of the ideal SiO_4 (or AlO_4) tetrahedron: 109.47°. The polarization is approximated by the core-shell model of Dick & Overhauser (1958)

$$U_p = k_p d^2 \tag{7}$$

where k_p is an atom-specific constant, and *d* is the core–shell separation.

Experimental

The material used here is from the Řečice granitic pegmatite.

Chemical analysis

Electron-microprobe analysis was done in wavelength-dispersion mode on a Cameca SX–50 instrument with a beam diameter of 5 μm and an accelerating potential of 15 kV. A sample current of 20 nA measured on a Faraday cup and a counting time of 20 s were used for Na, K, Ca, Mg, Al, Fe, Ti, Si and F, and 50 s at 40 nA for Rb, Cs, Sr, Ba, Zn, Sc and P. The following standards were used: albite (Na$K\alpha$), fayalite (Fe$K\alpha$), diopside (Ca$K\alpha$, Si$K\alpha$), kyanite (Al$K\alpha$), spessartine (Mn$K\alpha$), orthoclase (K$K\alpha$), zinnwaldite (F$K\alpha$), titanite (Ti$K\alpha$), olivine (Mg$K\alpha$), rubidian microcline (Rb$L\alpha$), gahnite (Zn$K\alpha$), pollucite (Cs$L\alpha$), apatite (P$K\alpha$), witherite (Ba$L\alpha$), $SrTiO_3$ (Sr$L\alpha$) and $NaScSi_2O_6$ (Sc$K\alpha$). The data were reduced using the PAP routine of Pouchou & Pichoir (1985).

Quantitative ion-microprobe analysis for Li, Be and B was done with a CAMECA IMS 4F instrument at C.N.R.–CSCC, Pavia, using a primary beam of $^{16}O^-$ ions (5–15 μm diameter) at 12.5 keV and 5–10 nA current intensity. Secondary ions at masses 7 (Li), 9 (Be), 11 (B), and 30 (Si) as the reference isotope for the matrix, were collected under an ion-imaged field 25 μm in diameter, contrast diaphragm of 400 μm, and field aperture of 1800 μm. Analytical reproducibility was checked on a standard sample (natural Macusani rhyolite glass), resulting typically in a few percent variation over the span of a day. Energy filtering was used to monitor secondary ions: medium- to high-energy ions of ~100 ± 25 eV energies were selected in this experimental configuration. This approach is very effective in minimizing matrix effects for the light lithophile elements, Li, Be and B, over a wide range of concentration (Ottolini *et al.* 1993). It is a particularly effective method for B, and careful experiments show that an accuracy of 3% relative is possible (Hawthorne *et al.* 1995). Further details of this method as applied to micas are given in Černý *et al.* (1994).

Collection of the powder-diffraction data

The sample was ground in alcohol to less than 10 μm using an automated grinder. A thin film of powder was spread (without solvent) on prolene over a circular area of ~10 mm in diameter, whose boundary was confined by a thin wire ring glued onto the prolene using hair spray. The thin film was finely serrated with a razor blade, and then carefully covered by prolene to fix the powder during data collection. Structure refinement of a sample of muscovite (of known structure) prepared in this fashion showed that preferred orientation is almost completely removed. Powder-diffraction intensity data were collected on a Siemens D5000 X-ray diffractometer in the 2θ range of 8–122° in steps of 0.02° 2θ with a step-counting time of 20 s. The instrument operates in transmission geometry with a curved Ge crystal incident-beam monochromator that provides a monochromatic beam of Cu$K\alpha_1$ radiation. A Kevex Psi-II solid-state (energy-dispersion) detector was used to record the diffracted radiation. Details of the data collection are listed in Table 1.

STRUCTURE REFINEMENT OF TWO POLYTYPES OF BOROMUSCOVITE

The refinement used the structure of Richardson & Richardson (1982) as a starting model for the $2M_1$ polytype, and the structure of Sidorenko *et al.* (1975) for the $1M$ polytype. Initial refinement was done using the modified Rietveld program LHPM3, originally written as DBW3.2 by Wiles & Young (1981) and modified by Hill & Howard (1986). In calculating the diffraction pattern, the background was fitted to a polynomial function. A pseudo-Voigt peak-shape function was used, in which the percentage Lorentzian character varied as a function of 2θ. The profile intensity was calculated over four FWHM on either side of each peak centroid. Isotropic displacement factors were fixed at the values of the starting structure-models. Details of the Rietveld refinement are summarized in Table 1. During structure refinement, when the atomic coordinates of the minor phase (the $1M$ polytype) were fixed, the structure of the dominant $2M_1$ phase could be refined, but resulted in unrealistic *T*–O distances. When attempting to refine the structure of the minor $1M$ phase, convergence could not be achieved. Structure-energy minimization of the $1M$ structure suggested the presence of a mirror plane, and refinement in the space group *C*2/*m* (rather than *C*2 of the starting model) did converge. However, unrealistic *T*–O distances occurred in both phases.

At this stage, we switched to the coupled method. The coefficients for the various potential functions (equations 4–7) are listed in Table 2. Isomorphous replacement, such as B → Si and Al → Si, was not

TABLE 1. INTENSITY DATA COLLECTION AND DETAILS OF STRUCTURE REFINEMENT

	$2M_1$	$1M$
a (Å)	5.090(1)	5.102(4)
b (Å)	8.822(2)	8.788(7)
c (Å)	19.819(5)	10.076(7)
β (°)	95.62(1)	101.23(3)
V (Å^3)	885.67	443.12
2*θ* scan range (°)	17–122	
step interval (°2*θ*)	0.02	
integration time/step (s)	20	
maximum intensity (counts)	1720	
Unique reflections	747	397
Structural parameters	38	24
Experimental parameters	12	
N-P	5177	
R_P	10.8	
R_{WP}	13.8	
R_{EXP}	7.9	
R_{BRG}	3.8	3.8

TABLE 2. POTENTIAL PARAMETERS USED IN THE STRUCTURE-ENERGY CALCULATION

	Short-range repulsion: Born/Buckingham-type potentials*			
	λ (kCal/mol)	*ρ* (Å)	C (kCal/mol·Å^{-6})	Ref
Si^{4+}–O^{2-}	29607.352	0.3025	245.860	[1]
Al^{3+}–O^{2-}	33675.03	0.29912		[2]
K^{1+}–O^{2-}	1505142.4	0.2134		[3]
H^{1+}–O^{2-}	30000	0.25		[4]
O^{2-}–O^{2-}	524946	0.149	642.9	[1]
	Bond-bending interaction**			
	k_B (kCal/rad^2)		θ_0 (°)	
O^{2-}–Si^{4+}–O^{2-}	48.3631		109.47	[1]
	Shell-core interaction between O-shell and O-core***			
		k_P (kCal/Å^2)		
O(core)$^{+0.86902}$–O(shell)$^{-2.86902}$		1728		[1]

* cf. equations 5 & 6; ** cf. equation 7; *** cf.equation 8

[1] Sanders *et al.* (1984); [2] James (1979); [3] Post & Burnham (1986); [4] Abbott *et al.* (1989).

considered in the energy calculation, except that an effective charge of 3.75+ (based on the chemical analysis) instead of 4+ was used for the *T* atoms in the calculation of Coulombic energy. The potential terms involving (Si,B,Al)–O, (Al,Mg)–O, and (K,Na)–O were approximated using parameterizations for Si–O, Al–O and K–O, respectively. The isomorphous replacements can be compensated for by the Rietveld part of the coupled method.

It should be emphasized here that the potential parameterization involves only Si, Al, K, H and O, and energy minimization alone would result in the muscovite structure. Thus information on the "boromuscovite" character of the sample (*i.e.*, short *T*–O distances, low *T*-site scattering, smaller unit-cell dimensions) come entirely from the Rietveld component of the coupled procedure. However, in the absence of the constraint of the energy minimization, the Rietveld refinement alone resulted in impossible individual *T*–O distances. Hence, it is apparent that the constraints of the energy minimization play an important role in the extraction of the boromuscovite features of the sample from the X-ray data *via* Rietveld refinement.

RESULTS

The chemical composition and unit formula of boromuscovite are listed in Table 3. The refined atomic positions are shown in Table 4, selected bond-distances and angles are listed in Table 5, and site occupancies are given in Table 6. The overall fit between the calculated and the observed diffraction-patterns is shown in Figure 1.

TABLE 3. CHEMICAL COMPOSITION (wt%) AND UNIT FORMULA OF BOROMUSCOVITE

	1	2		1	2
SiO_2	48.21	48.1			
Al_2O_3	29.19	28.1	Si	3.10	3.06
B_2O_3	6.12	7.0	Al	0.22	0.16
FeO	0.04	0.1	B	0.68	0.78
MnO	-	0.08			
MgO	0.03	0.15	Al	1.99	1.94
BaO	0.11	--	Mg	-	0.01
CaO	-	0.01	Li	0.01	0.01
Li_2O	0.03	0.05			
K_2O	10.93	11.0	Ca	-	0.01
Na_2O	0.06	--	K	0.89	0.89
Rb_2O	0.03	0.52	Rb	-	0.01
Cs_2O	0.02	0.05	Na	0.01	--
H_2O	4.61**	4.77			
F	0.11	0.76	O	10	10
O=F	-0.05	0.32	OH	1.98	2.02
Total	99.44	100.46	F	0.02	0.16

1. Present work, sample from Řečice, Czech Republic. 2. Foord *et al.* (1991), sample from the Little Three mine, California, P, Ti, Sc, Sr, Zn, Be, Mn not detected. **Estimated by stoichiometry. -: not detected, --: not determined.

TABLE 4. FINAL ATOMIC COORDINATES OF BOROMUSCOVITE POLYTYPES

	x	*y*	*z*	Displacement factor
		$2M_1$ polytype		
A1	0.25 (3)	0.079(2)	-0.0002(7)	0.47
T1	0.442(3)	0.254(2)	0.1351(7)	0.12
T2	0.045(3)	0.426(2)	0.3640(7)	0.17
K	0	.103(2)	1/4	0.26
O	0.039(5)	0.072(4)	0.4541(6)	0.35
O1	0.385(5)	0.248(4)	0.0569(12)	0.37
O2	0.043(4)	0.438(3)	0.4466(13)	0.29
O3	0.419(4)	0.090(3)	0.1655(10)	0.38
O4	0.229(6)	0.361(3)	0.1636(10)	0.68
O5	0.270(5)	0.314(2)	0.3466(12)	0.32
		1*M* polytype		
Al	0	0.666(8)	0	0.62
T	0.437(11)	0.674(5)	0.272(5)	0.12
K	1/2	0	1/2	0.26
OH	0.433(16)	0	0.100(8)	0.35
O1	0.347(12)	0.715(6)	0.116(8)	0.37
O2	0.192(14)	0.726(7)	0.33 (8)	0.68
O3	0.520(17)	1/2	0.287(9)	0.38

The chemical composition is very similar to that reported by Foord *et al.* (1991). The structural formula of the Řečice boromuscovite, calculated on the basis of 12 [O + OH + F], is $(K_{0.89}Na_{0.01})(Al_{1.99}Li_{0.01})(Si_{3.10}B_{0.68}Al_{0.22})\,O_{10.0}[(OH)_{1.98}F_{0.02}]$. The cell dimensions for both $2M_1$ and $1M$ polytypes are similar to those given by Foord *et al.* (1991). Based on the refined cell parameters and scale factors of the two polytypes in the powder, the relative weight percentage of the $2M_1$ polytype can be calculated from the formula of Hill & Howard (1987):

$$W_{2M1} = \frac{S_{2M1}\,(ZMV)_{2M1}}{S_{2M1}\,(ZMV)_{2M1} + S_{1M}\,(ZMV)_{1M}} \cdot 100\% \qquad (8)$$

in which *S*, *Z*, *M* and *V* are the refined scale-factor, number of formula units in the unit cell, the mass of the formula unit, and the cell volume, respectively. The results of the present refinement give W_{2M1} = 83 wt% and W_{1M} = 100 − 83 = 17 wt%. This result differs significantly from that of Foord *et al.* (1991), who gave a 50:50 ratio of the two polytypes in the mixture from the Little Three mine, California.

DISCUSSION

In the $2M_1$ polytype, the $<T1–O>$ distance is slightly shorter than the $<T2–O>$ distance (Table 5). The difference arises from the different $T–O_{nbr}$ distances. The $T1–O_{nbr}$ is shorter, whereas $T2–O_{nbr}$ is greater than $T–O_{br}$, respectively. The $T–O_{br}$ distances are similar within individual polytypes and between polytypes, and are close to 1.57 Å. The refined *T*-site occupancies for (Si+Al) and B agree well with results of the chemical analysis. On a plot relating B-content and

TABLE 5. INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN BOROMUSCOVITE

$2M_1$ POLYTYPE			
T1-O1	1.55(2)	T2-O2	1.64(2)
T1-O3	1.58(3)	T2-O3c	1.58(3)
T1-O4	1.58(3)	T2-O4e	1.56(3)
T1-O5	1.57(2)	T2-O5	1.57(3)
<T1-O>	1.57	<T2-O>	1.59
O1-O3	2.56(4)	O2-O3c	2.62(4)
O1-O4	2.53(3)	O2-O4e	2.56(3)
O1-O5	2.53(4)	O2-O5	2.63(3)
O3-O4	2.58(4)	O3c-O4e	2.57(4)
O3-O5	2.56(4)	O3c-O5	2.62(4)
O4-O5	2.61(4)	O4e-O5	2.56(4)
<O-O>T1	2.56	<O-O>T2	2.59
O1-T1-O3	109.8(21)	O2-T2-O3c	108.9(17)
O1-T1-O4	108.2(14)	O2-T2-O4e	106.1(14)
O1-T1-O5	108.6(13)	O2-T2-O5	109.5(14)
O3-T1-O4	109.4(13)	O3c-T2-O4e	109.8(16)
O3-T1-O5	108.8(15)	O3c-T2-O5	112.5(15)
O4-T1-O5	112.0(16)	O4e-T2-O5	109.6(15)
<O-T1-O>	109.5	<O-T2-O>	109.4
Al-O1	1.96(3)	K-O3 x2	2.84(2)
Al-O1a	1.98(3)	K-O4g x2	2.99(2)
Al-O2b	1.91(2)	K-O5 x2	2.92(2)
Al-O2c	1.88(3)	<K-O$_{inner}$>	2.92
Al-OHd	1.89(3)		
Al-OH	1.81(2)	K-O3f x2	3.25(2)
<Al-O>	1.90	K-O4 x2	3.14(2)
		K-O5g x2	3.46(2)
		<K-O$_{outer}$>	3.28
$1M$ POLYTYPE			
T-O1	1.59(7)	Al-O1	1.97(6)
T-O2	1.56(7)	Al-O1i	1.85(8)
T-O2h	1.59(7)	Al-OHj	1.84(6)
T-O3	1.59(5)	<Al-O>	1.89
<T-O>	1.58		
O1-O2	2.46(9)	O1-T-O2	103(4)
O1-O2h	2.57(10)	O1-T-O2h	108(4)
O1-O3	2.60(10)	O1-T-O3	110(4)
O2-O2h	2.59(2)	O2-T-O2h	110(4)
O2-O3	2.69(9)	O2-T-O3	118(5)
O2h-O3	2.57(8)	O2h-T-O3	108(4)
<O-O>T	2.56	<O-T-O>	109.5
K-O2k x4	3.17(6)		
K-O2l x4	2.90(7)		
K-O3m x2	2.92(9)		
<K-O>	3.00		

a: 1/2-x, 1/2-y, -z; b: 1/2+x, 1/2-y, 1/2+z; c: 1/2-x, 1/2+y, 1/2-z; d: x, -y, -1/2+z; e: -x, y, 1/2-z; f: 1-x, y, 1/2-z; g: 1/2-x, -1/2+y, 1/2-z; h: 1/2+x, 1/2-y+1, z; i: 1/2-x, 1/2-y+1, -z; j: 1/2-x, 1/2+y, -z; k: x, 1-y, z; l: 1/2+x, 1/2+y, z; m: -1/2+x, -1/2+y, z.

TABLE 6. REFINED SITE-OCCUPANCIES AND ASSIGNED SPECIES IN BOROMUSCOVITE POLYTYPES

	Refined occupancy	Assigned from formula unit
	$2M_1$ polytype	
Al	0.96(2) Al	1.99 Al
T1	0.78(3) Si + 0.22(3) B	3.10 Si + 0.22 Al + 0.68 B
T2	0.72(3) Si + 0.28(3) B	
K	0.41(1) K	0.89 K
	$1M$ polytype	
Al	0.41(5) Al	1.99 Al
T	0.75(13) Si + 0.25(13) B	3.10 Si + 0.22 Al + 0.68 B
K	0.20 K	0.89 K

<*T*–O> distance, the *T*1 and *T*2 sites fall on the trend suggested by Fleet (1992). The <*T*–O> distance (1.58 Å) in the $1M$ polytype is equal to the average of those in the $2M_1$ polytype, indicating no preferred partitioning of B into either polytype. The refined *T*-site occupancy of (Si+Al) is not as reliable as those in the $2M_1$ polytype, as there was strong correlation between the site occupancy and scale factor during refinement.

SUMMARY

(1) Boromuscovite from a granitic pegmatite at Řečice, Czech Republic, is a mixture of 83 wt% $2M_1$ and 17 wt% $1M$ polytypes.

(2) Crystal structures of both polytypes were successfully refined using the coupled Rietveld – static-structure energy-minimization method. Simultaneous refinement of the structures of the two polytypes converged to R_{wp} = 13.8% (R_{exp} = 7.9%), R_{BRG} ($2M_1$) = 3.8% and R_{BRG} ($1M$) = 3.8%.

(3) The coupled Rietveld – static-structure energy-minimization method allows much more accurate determination of modal amounts and crystal-structure details of mixtures of polytypes than has hitherto been possible.

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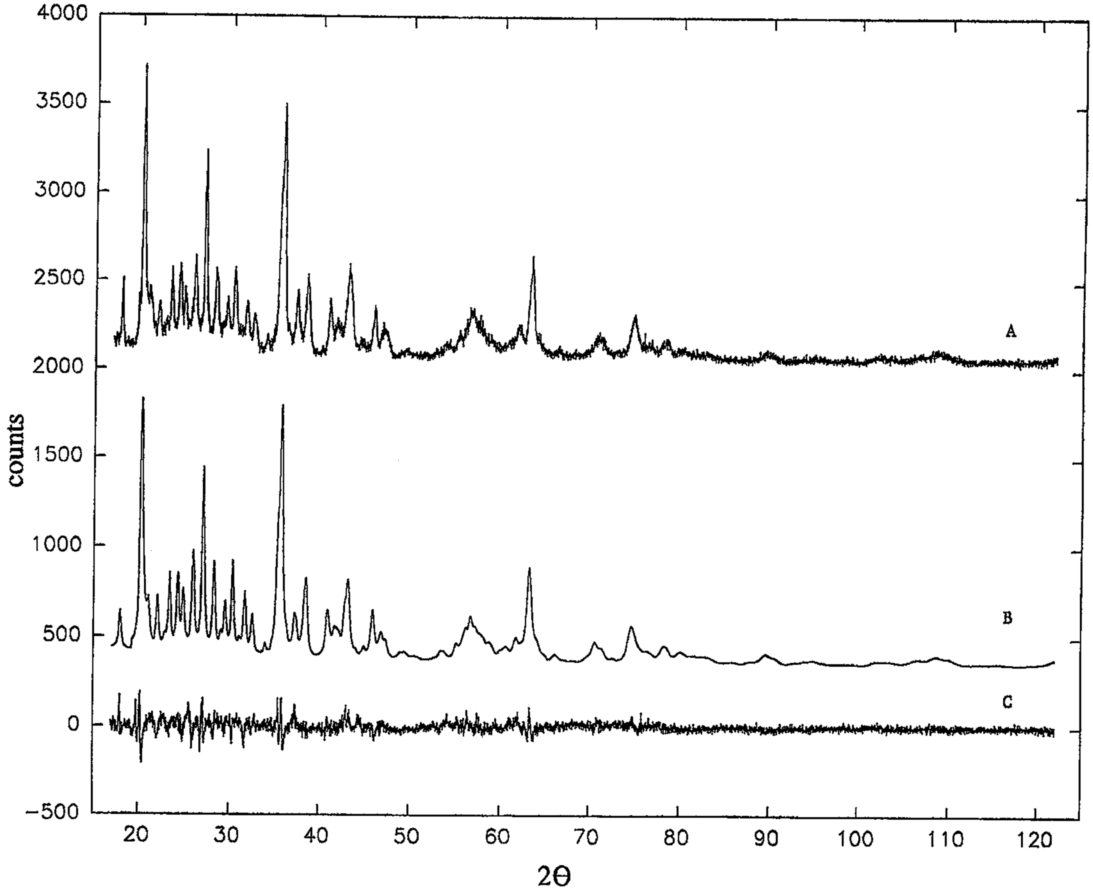

FIG. 1. A. Observed pattern. B. Calculated pattern. C. Difference between the two.

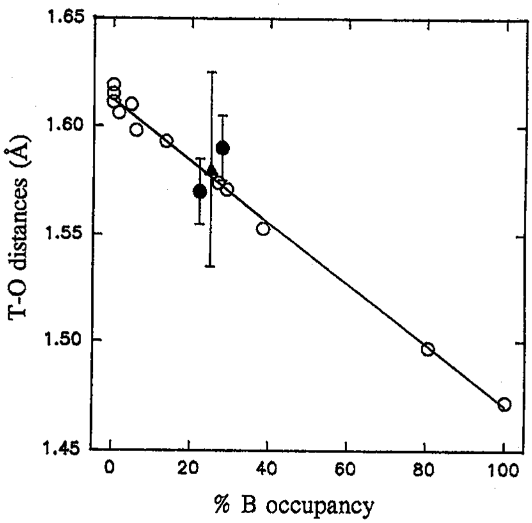

FIG. 2. The relationship between <*T*–O> distances and B content; solid circle: boromuscovite ($2M_1$); solid triangle: boromuscovite (1*M*); open circle: data points from Fleet (1992); line: linear regression of data points from Fleet (1992).

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